perspective

Perspective Note **PS05**

Carbonate Δ47 'Clumped Isotope' Measurement Using the Perspective and Nu Carb Carbonate Preparation Unit in 'Micro-Volume' Mode

- **Routine Δ47 measurement of carbonates**
- **Wide range of sample weights (150 Qg- 6 mg)**
- **Δ47 precision< 0.02‰ in 'micro-volume' mode**

The Nu Perspective IS coupled to the Nu carb carbonate preparation unit allows precise and accurate measurements of isotopic 'clumping' in carbonates over a wide range of sample size (150 vg to 6 mg). The Nu carb uses acid digestion of carbonates to liberate CO_2, which is first dried by passage through a cryogenic water trap (-90 °C), then purified by transit through an adsorption trap (-30 °C). The adsorption trap is fully software controlled and can be baked and cooled automatically.

Figure 1: Nu carb with dual inlet and adsorption trap

The large range in measurable sample size is achieved by using the dual inlet bellows for large samples (> 3 mg), and using precisely matched sample and reference 'micro-volumes' for small samples (150 µg to 3 mg). The 'micro-volumes' allow the gas to deplete into the Perspective IS source at a precisely matched rate. The 'micro volumes' also have a larger volume than used for conventional carbonate analysis (δ13C, δ180), allowing a full Δ7 analysis (50 min) to take place using a single sample (60 sample/reference changeovers, each lasting 20 s, with a 6 s delay after each changeover).

Before the acquisition, depending on the amount of gas detected by the Perspective IS, the sample is automatically expanded into a larger (> 350 µg carbonate) or smaller (< 350 µg carbonate) 'micro-volume'. Typically, a 500 vg carbonate sample will be too large for the small 'micro-volume', and will be 'chopped' into the larger volume. For example 500 vg of carbonate yields about 70 nA (14 V) 44 signal, which will then deplete down to 30 nA (6 V) during the acquisition. Very much larger samples (> 3mg) are expanded into the dual inlet bellows.

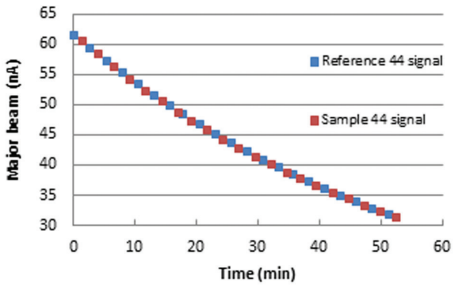

Figure 2: 'Micro-volume' depletion during an analysis of a 500 pg Carrara marble sample. Closely matched sample and reference beams deplete from 12.4 V to 6 V 44 signal.

An example of the range of sample weights that can be analysed is given in below:

Weight (µg)	Chops	Raw Δ46 (‰	Raw Δ47 S.E. (‰)
165	0	-0.674	0.014
166	0	-0.614	0.017
211	0	-0.665	0.013
250	0	-0.690	0.012
274	0	-0.706	0.012
286	0	-0.679	0.012
301	0	-0.685	0.010
354	1	-0.742	0.010
382	0	-0.704	0.009
393	1	-0.685	0.012
398	1	-0.707	0.011
425	1	-0.685	0.010
524	1	-0.704	0.008
Average		**-0.688**	
Standard Dev.		**0.029**	

Figure 3: 'ETH-2' standard run with weight 160— 530 pg. "0 Chops"; small 'micro-volume' used. "1 chop"; large 'micro-volume' used

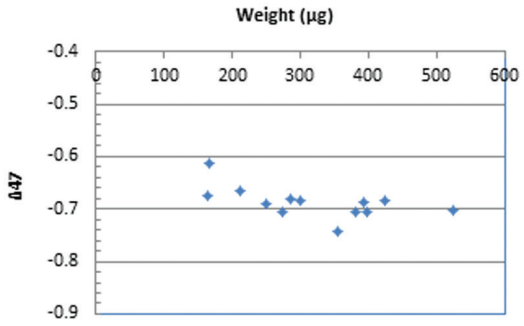

Figure 4: 'ETH-2' standard run with weight 160 — 530 pg. Precision of 0.03‰ over entire weight range.

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To calibrate the values produced by the Perspective IS and Nu carb, CO_2 standards of different isotopic composition were 'scrambled' by heating the gas to 1000 °C in quartz tubes, and also equilibrated above water at different temperatures. The resulting gas was prepared in small volumes equivalent to the gas produced by a 500 vg carbonate sample. This gas was introduced such that it underwent the same cleanup as a Nu carb sample and was run out of the dual inlet 'micro-volume'. The resulting heated and equilibrated 'gas lines' are shown below.

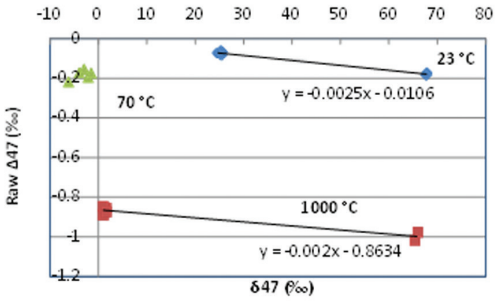

Figure 5: Heated gas (1000 °C) and equilibrated gas lines (23 °C and 70 °C).

After linearizing the heated gas data, a 'transfer function' was created by plotting the accepted theoretical values for M7 against the measured M7 values:

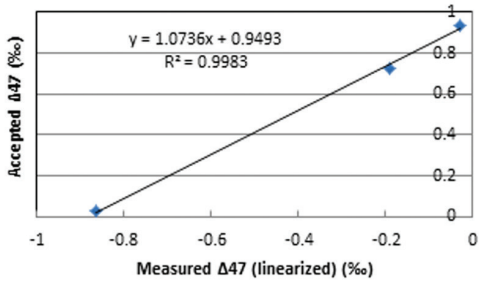

Figure 6: Transfer function using the theoretical values for heated and equilibrated gases.

A series of carbonate standards were then run to obtain their raw M7 values. These results were first linearized using the gradient of the 'heated gas line' (-0.002). This corrects for small changes in the measured raw M7, dependent on the isotopic composition of the CO_2. The transfer function was then applied to the linearized raw A 47 values, transforming them into the absolute reference frame (ARF) as per Dennis et al. [(1)]. It was necessary to add an acid fractionation correction of 0.064‰ (Meckler et al. [(2)]) to the data. This data is shown below.

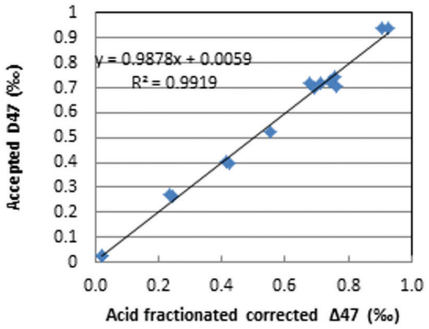

Figure 7: Accepted 447 values plotted against measured values transformed into the ARE Heated and equilibrated gas values are also plotted.

Conclusion:

These results show that the Nu carb coupled to the Perspective IS can yield precise and accurate measurement of 'clumping' in carbonates over a wide range of sample size.

References:

(1) Dennis K. J., Affek H. P., Passey B. H., Schrag D. P., Eller J. M. Defining an absolute reference frame for 'clumped' isotope studies of CO2. Geochimica et Cosmochimica Acta 75 (2011) 7117-7131

(2) Meckler A. N., Ziegler M., Milian M. I., Breitenbach S. F M., Bernasconi S. M. Long-term performance of the Kiel carbonate device with a new correction scheme for clumped isotope measurements. Rapid Commun. Mass Spectrom. 28 (2014) 1705-1715A

*Standards provided by H. P Affek, S. M. Bernasconi, A. Tripati and W F Defliese.

Sample	avg. weight (µg)	δ47 avg. (%)	Δ47 raw avg. (‰)	Δ47 abs avg. (‰)	Δ47 acid frac. corr +0.64 (‰)	standard deviation (‰)	Number of samples	expected Δ47 (‰)	Difference (‰)
NCM	559	70.541	-0.691	0.362	0.426	0.022	2	0.395	-0.031
Carmel chalk	557	64.601	-0.429	0.631	0.695	0.014	2	0.697	-0.002
YCM	538	70.736	-0.704	0.349	0.413	0.012	5	0.404	0.009
ETH 1	510	70.304	-0.857	0.183	0.247	0.004	2	0.267	-0.020
ETH 2	541	39.772	-0.806	0.171	0.235	0.009	5	0.269	-0.034
ETH 3	530	71.015	-0.379	0.698	0.762	0.012	3	0.705	0.057
ETH 4	543	40.310	-0.512	0.488	0.552	0.013	3	0.524	0.028
45a oyster	570	69.980	-0.383	0.691	0.755	0.021	3	0.741	0.015
52 oyster	535	59.563	-0.403	0.647	0.711	0.011	3	0.715	-0.004
9-25-G	542	55.596	-0.427	0.613	0.677	0.010	3	0.717	-0.040